Characterization of anisotropic particles by rheo-optics

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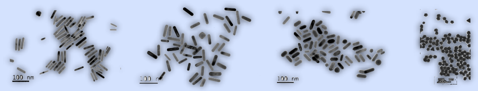
Abstract

Anisotropic nanoparticles are being increasingly used in many applications. Presently, dimensions of nanoparticles are mainly obtained by transmission electron microscopy (TEM). The average dimensions from TEM are obtained by image analysis of a few hundred particles, resulting in poor statistical average. Also, microscopy does not provide any information on the hydrodynamic dimensions. For studies of dynamical properties such as sedimentation or rheology, hydrodynamic dimensions of the particle are more important than the actual physical dimensions. In the present work, a rheo-optical technique (dichroism) is used, which gives a faster and better statistical average of the hydrodynamic aspect ratio and the associated polydispersity. Results obtained from dichroism for stiff gold rods and gold decahedrons will be presented. Results for gold rods will be compared to those obtained from TEM and dynamic light scattering (DLS).

TEM

GoldRod-1 *GoldRod-2* *GoldRod-3* *GoldDisk*



Sample	*L (nm)*	*W (nm)*	*AR$_{TEM}$*
GoldRod-1	*56,26±5,83*	*20,86±2,94*	*2,76±0,52*
GoldRod-2	*61,66±7,18*	*18,16±0,47*	*3,43±0,47*
GoldRod-3	*66,69±6,14*	*15,61±1,93*	*4,33±0,65*
GoldDisk	*50*	*100*	*0,5*

Dynamic Light Scattering

Rotational diffusion **Translational diffusion**

$$I(Q,\omega) = I_{iso}(Q,\omega) + I_{aniso}(Q,\omega)$$

$$I(Q,\omega) \propto S(Q,\omega)$$

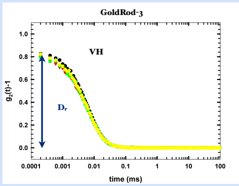
D_r

Auto correlation function

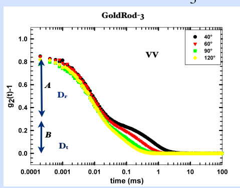
$$g_1(t) = \tilde{S}_{iso}(Q,t) + \tilde{S}_{aniso}(Q,t)$$

D_{II} $D_\perp$

$$\bar{D}_{avg} = \frac{2D_{II} + D_\perp}{3}$$



Rotational



Translational + Rotational

Method-1

$$\frac{A}{B} \propto f(\alpha_{11},\alpha_\perp) \propto f(L,d)$$

$$\frac{A}{B} = \frac{5}{4}\frac{{\alpha_{11}}^2}{\langle(\alpha_\perp - \alpha_{11})^2\rangle}$$

Sample	*AR*	
	Method-1	*Method-2*
GoldRod-1	*2,58*	*2,22*
GoldRod-2	*3,19*	*2,66*
GoldRod-3	*3,43*	*3,16*

Method-2

$$D_r = \frac{3k_BT(\ln(L/d_{cs}) + C_r)}{\pi\eta L^3}$$

$$\bar{D} = \frac{k_BT(\ln(L/d_{cs}) + \bar{C})}{3\pi\eta L}$$

Pecora, R. *J. Chem. Phys.* **1968**, 49, 1036

Broersma S. *J. Chem. Phys.* **1960**, 32, 1626,1632

Ortega A. Garcia de la Torre *J. Chem. Phys.* **2003**, 119, 9914

Jessica, R. et al., *J. Phys. Chem. C* **2007**, 111, 5020

Rheo-optics

Dichroism

The difference between the imaginary parts of the refractive indices of the medium measured parallel and perpendicular to the average particle orientation $\Delta n'' = n''_{11} - n''_\perp$

$$\Delta n'' = \frac{\delta''\lambda}{2\pi d}$$

δ'' *Extinction coefficient*

λ *Wave length of light*

d *Optical path length*

χ *Orientational angle*

r *Particle aspect ratio*

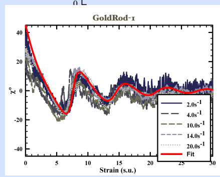
Flow start up

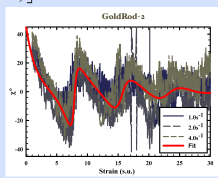
Tumbling

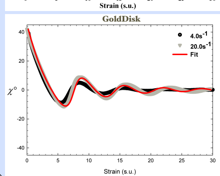
$$\tan 2\chi = \frac{2\int_0^\infty (r - r^{-1})\sin\left(\frac{4\pi t}{T}\right)g(r)dr}{\int_0^\infty \left[(r^2 - r^{-2}) - (r^2 - r^{-2})\cos\left(\frac{4\pi t}{T}\right)\right]g(r)dr}$$

Tumbling period

$$T = \frac{2\pi}{\dot{\gamma}}(r + \frac{1}{r})$$







Sample	*Dichroism*	
	AR	*Polydispersity*
GoldRod-1	*1,7*	*0,6*
GoldRod-2	*2,0*	*0,6*
GoldRod-3	*-*	*-*
GoldDisk	*0,556*	*0,7*

Fuller, G. G., *Optical Rheometry of Complex Fluids*, Oxford Univ. Press Oxford (1995)

Vermant, J. et al., *AIChE.* **2001**, 47, 790

Conclusions

- **TEM - only physical aspect ratio (less statistics)**
- **DLS - hydrodynamic aspect ratio**
  - **Assumption - stabilizing layer thickness (method-1)**
  - **Method-2 can be used only for 2>AR<20**
  - **No information about polydispersity**
- **Rheo-optics - hydrodynamic aspect ratio and polydispersity**
  - **Assumption - ellipsoid - small aspect ratio**
  - **Pe number should be high**

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